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Final Report on
Project Number NR-057-233
Contract Nonr-03700
under the direction of Edward S. Amis

by

Edward S. Amis

University of Arkansas

Department of Chemistry

January 25, 1964

Fayetteville, Arkansas

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The following graduate students have been employed on the project investigating the phases indicated.

James Lee Hockersmith, "The Dielectric Constant and Salt Effects upon the Acid Hydrolysis of Methyl Propionate." This work resulted in Technical Report No. 2, dated October 25, 1952, and in a publication in *Analytica Chimica Acta* 9, 101 (1953). Mr. Hockersmith received his M. S. Degree from the University of Arkansas in February 1952. His thesis for the degree was taken from work done on the project.

J. M. Cothron, "The Acid Hydrolysis of Ethyl Acetate in Acetone-Water Mixtures. Mr. Cothron resigned his assistantship on the project after only one semester.

Mr. P. Madhavan Nair, "The Dielectric Constant Effect upon the Acid Hydrolysis of Ethyl Acetate." This work was presented in Technical Report No. 3 of October 28, 1952 and in *Analytica Chimica Acta* 9, 111 (1953).

Mr. Nair is continuing work on substituted esters. A technical report on this work to date is enclosed.

Mr. Nair's work will be used as a dissertation in partial fulfillment for the degree of Doctor of Philosophy at the University of Arkansas.

Mr. Navin P. Shah, "The Dielectric Constant and Salt Effects upon the Acid Hydrolysis of Ethyl Formate." Technical Report No. 4, dated November 25, 1952 was taken from this

work which will be presented in the near future, perhaps to the Journal of the American Chemical Society for consideration for publication. Mr. Shah is working toward the Ph. D. Degree.

Mr. John E. Quinlan, "The Dielectric Constant Effect upon the Alkaline Hydrolysis of Methyl Propionate." From this work Technical Report No. 6, dated November 10, 1953 was written. The work will be used in partial fulfillment of the requirements for the Master of Science degree at the University of Arkansas in June, 1954. It is planned to present the work for publication, perhaps to the Journal of the American Chemical Society.

In addition to the graduate assistants mentioned above, the author has spent much time on the contract. He is joint author of Technical Reports Numbers 2, 3, 4, and 6 mentioned above and has alone authored Technical Reports Numbers 1 and 5. He has also published the following papers for which the contract with the Office of Naval Research is given credit.

1. Concerning Edmonds and Birnbaum's Equation for the Equilibrium Constant for the Formation of a Colored Complex," J. Am. Chem. Soc., 74, 1340 (1952).
2. Coulomb's Law and the Quantitative Interpretation of Reaction Rates," J. Chem. Educ., 29, 337, 1952.
3. Coulomb's Law and the Quantitative Interpretation of Reaction Rates, II," J. Chem. Educ., 30, 351 (1953).

Paper III in the Coulomb's Law Series has been presented for consideration for publication.

The stated purpose of the work when the contract was granted was to check, using data on both acid and alkaline hydrolysis of esters, existing equations for the dielectric constant and ionic strength effects upon the rates of ion-dipolar molecule reaction rates.

Equations by Laidler and Eyring (Ann. New York Acad. Sci., 39, 299 (1940)) and by Amis and Jaffe (J. Chem. Phys., 10, 598 (1942)) agree in their predictions with respect to the dielectric constant and ionic strength effects upon reactions between positive ions and dipolar molecules. The equations make opposite predictions with respect to these effects for reactions between negative ions and dipolar molecules.

The results of the experimental data on esters taken under this contract confirm the directions of the dielectric constant effects as predicted by the Amis-Jaffe equation. The ionic strength effect proved to be a catalytic rather than an ion-atmosphere effect.

More important, simpler equations have been derived for the effect of dielectric constant upon rates of reactions between various charge types of chemical reactants using the Coulomb's law approach. The resulting equation in the case of reactions between ions and ions is identical with that derived by Scatchard using the Christiansen intermediate complex approach. The equation for the ion-dipolar molecule reaction type agrees in the prediction of the directions of

the effect with the Amis-Jaffe equation but the new equation is simpler to derive and apply and gives a straight line dependence of the logarithm of the specific rate constant upon the reciprocal of the dielectric constant.

The derivation and verification of the equations were presented in the two papers by Amis published in the J. Chem. Educ. and in the paper now being considered for publication. The two published papers have received wide notice and reprints of these papers have been requested by scientists in the leading laboratories and universities of this country and by scientists in England, Ireland, Wales, Italy, Yugoslavia, Germany, Japan, India, Australia, and other foreign lands.

To summarize, the principal contributions of the contract has been to:

- A. Support worthy, capable graduate students in their efforts to secure advanced degrees.
- B. Support fundamental research which the university was unable to support adequately.
- C. Make possible the checking of the predictions of existing equations concerning the dielectric constant and salt effects upon ion-dipolar molecule reaction rates as exemplified by both the acid and alkaline hydrolysis of esters.
- D. Make possible a new approach to the dielectric constant effects upon the rates of reaction between various charge types of reactants.

The author wishes to express his deep gratitude to the Office of Naval Research for its support of his research

program under Contract Nonr-03700. He also wishes to commend the Office of Naval Research for the freedom of action and of choice which the author experienced under this contract and for the democratic way in which the contract was administered. It is with deep regret that the author sees the contract terminated.